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THEORY OF DISTILLATION

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Distillation is one of the more important operations you will perform in the organic chemistry laboratory. It is important that you understand some of the physical principles working during a distillation. Different systems require different treatments; the explanations that follow parallel the classifications of distillations given earlier in the book.

CLASS 1: SIMPLE DISTILLATION

In a simple distillation, you recall, you separate liquids boiling **BELOW** 150°C at 1 atm from

1. Nonvolatile impurities.
2. Another liquid boiling at least 25°C higher than the first. The liquids should dissolve in each other. If they do not, then you should treat the system like a steam distillation, and if you're going to steam distill, be sure to look at the discussion for Class 4: Steam Distillations. The boiling points should have a 25°C difference because you may assume the higher boiling component doesn't do anything but sit there during the distillation. Otherwise, you may have a two-component system, and you also need to look at the discussion for Class 3: Fractional Distillation, as well as the discussion here.

That said, let's go on with our discussion of the distillation of one-component systems.

Suppose you prepared isobutyl alcohol by some means, and at the end of the reaction you wound up with a nice yellow-brown liquid. Checking any handbook, you find that isobutyl alcohol is a colorless liquid that boils at 108.1°C at 760 torr. On an STP day, the atmospheric pressure (P) is 760 torr and the boiling point is the **normal boiling point**. At that point, the single point when the vapor pressure of the liquid is the same as that of the atmosphere, the liquid boils.

Fearing little, you set up a Class 1, Simple Distillation and begin to heat the mix. If you kept track of the temperature of the *liquid* (and you don't; the thermometer bulb is up *above* the flask) and its *vapor pressure*, you'd get the temperature-vapor pressure data in columns 1 and 2 of Table 1.

At 82.3°C the vapor pressure of the liquid is 290.43 torr—much *lower* than atmospheric pressure. The liquid doesn't boil. Heat it to, say, 103.4°C, and the vapor pressure is 644.16 torr. Close to atmospheric pressure but no

prize. Finally, at 108.1°C we have 760.04 torr. *The vapor pressure of the liquid equals that of the atmosphere, and the liquid boils.*

Now, do you see an entry in the table for brown gunk? Of course not. The brown gunk *must* have a very low (or no) vapor pressure at any temperature you might hit during your distillation. Without a vapor pressure, there can be no vapor. No vapor and there's nothing to condense. Nothing to condense, and there's no distillation. So the isobutyl alcohol comes over clean and pure, and the brown gunk stays behind.

If you plot the temperature and vapor pressure data given in Table 1, you reconstruct the **liquid-vapor equilibrium line** in the **phase diagram** of that liquid (Fig. 174). The equation of this line, and you might remember this from your freshman chemistry course, is the *Clausius–Clapeyron* equation:

$$p = p^0 \exp \left\{ \frac{-\Delta H}{R} \left(1/T - 1/T^0 \right) \right\}$$

Clausius and Clapeyron

So if you want to know how the vapor pressure of a substance is going to vary with temperature, you can use the *Clausius–Clapeyron* equation:

Table 1 Temperature–Vapor Pressure Data for Isobutyl and Isopropyl Alcohols.

Temperature (C°)	Isobutyl alcohol (torr)	Isopropyl alcohol (torr)
82.3	290.43	760.00
83.2	301.05	786.31
85.4	328.41	853.90
86.9	348.27	902.76
88.7	373.46	964.52
90.0	406.34	1044.83
95.8	488.59	1244.30
99.9	567.96	1435.11
103.4	644.16	1616.99
106.2	711.23	1776.15
108.1	760.04	1891.49

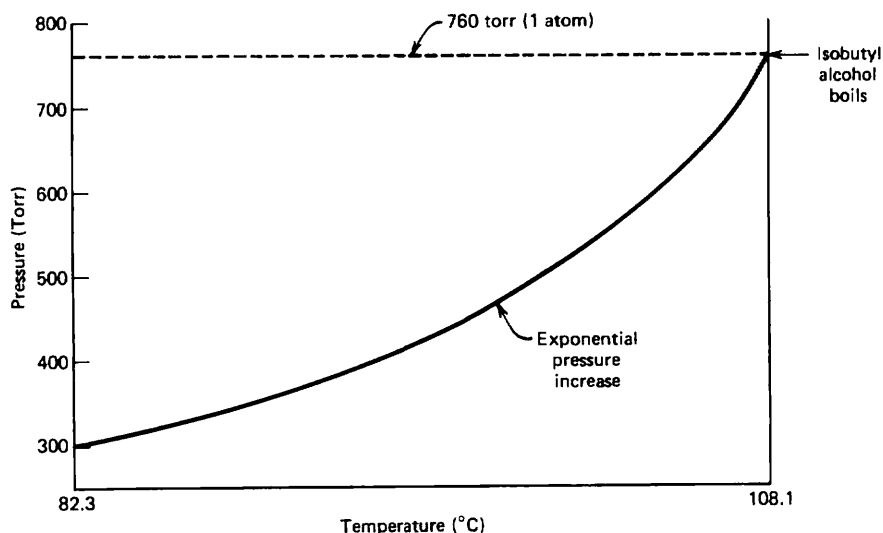


Fig. 174 Vapor pressure versus temperature curve for isobutyl alcohol.

$$p = p^{\circ} \exp \left\{ \frac{-\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T^{\circ}} \right) \right\}$$

where

p° is a known vapor pressure

T° is the known temperature (in K, *not* °C)

These are usually taken from the normal boiling point.

H is the heat of vaporization of the liquid.

R is the universal gas constant (8.314 J/mole-K).

T is the temperature you want the vapor pressure for.

p is the vapor pressure that you calculate for the temperature you want, T.

I've put this formula to two uses:

1. From the normal boiling point of isobutyl alcohol ($T^{\circ} = 108.1^{\circ}\text{C}$, 381.2K; $p^{\circ} = 760$ torr) and one other vapor pressure measurement that I found while doing research for this section ($T = 100^{\circ}\text{C}$, 373K; $p = 570$ torr), I've gotten the **heat of vaporization (H)**. This is the heat needed to vaporize a mole of pure isobutyl alcohol itself. Using these two values

in the Clausius–Clapeyron equation, I found that the H for isobutyl alcohol is 10039.70 cal/mole.

- Now, with the H for isobutyl alcohol, I've calculated the field of pressures you see in Table 1 from temperatures of 82.3 to 108.1°C. *That's why the last pressure at 108.1 is 760.04, and not 760.00. The 760.04 value has been back-calculated using the H that we calculated from the top pressure-temperature points in the first place.*

I've also listed the vapor pressure data for isopropyl alcohol in column 3 of Table 1. Again, two steps were required to generate the data:

- Two known vapor pressure-temperature points ($T^b=82.3^\circ\text{C}$, 355.4K, $p^o=760$ torr; $T=100^\circ\text{C}$, 373K, $p=1440$ torr) were used to calculate the H : 9515.73 cal/mol.
- Now that H for isopropyl alcohol, and temperatures from 82.3 to 108.1°C, were used to calculate a field of vapor pressures for isopropyl alcohol. These are in column 3 of Table 1.

I've done these calculations for several good reasons:

- To show you how to use the Clausius–Clapeyron equation, and to show you how well the equation fits over small temperature ranges. The calculated boiling point pressure for isobutyl alcohol (760.04 torr) is not very different from the normal boiling point pressure of 760.00 torr (0.005%).
- To show you that compounds with *higher H 's have lower vapor pressures*. This means that it takes more energy to vaporize them.
- To show you that you can calculate vapor pressures that are *above* the boiling point of the liquid. They have a slightly different meaning, however. There is no liquid isopropyl alcohol at 100°C and 760 torr. The vapor pressure at 100°C is 1440 torr, almost twice the atmospheric pressure. But if we artificially increased the pressure over a sample of isopropyl alcohol (pumped up the flask with compressed air?) to 1440 torr and then heated the flask, the alcohol would no longer boil at 82.3°C. You'd have to go as high as—did someone say 100°C—before the vapor pressure of the liquid matched the now pumped-up atmospheric pressure, and the liquid would boil.
- To show you the theory of the next topic, Class 3: Fractional Distillation.

CLASS 3: FRACTIONAL DISTILLATION

In a fractional distillation, you remember, you are usually separating liquid mixtures, soluble in one another, that boil at less than 25°C from each other at a pressure of one atmosphere.

Now I didn't discuss *both* isopropyl and isobutyl alcohol in the last section for my health. Suppose you're given a mixture of these two to separate. They *are* miscible in each other, and their boiling points are just about 25°C apart. A textbook case, eh?

A Hint from Dalton

So you set up for a fractional distillation and begin to heat the liquid mixture. After a bit, it boils. And what does that mean? The vapor pressure of the *solution* (not just one component) is now equal to the atmospheric pressure, 760 torr. (We're very lucky that textbook-land has so many STP days.) Each component exerts its own vapor pressure, and when the *total* pressure reaches 760 torr, the solution boils.

$$P_{\text{Total}} = P_A + P_B$$

This is **Dalton's law of partial pressures**. The total pressure of the gang is equal to the sum of their individual efforts. Here, A could be the isopropyl alcohol and B the isobutyl (it doesn't matter), but P_{Total} must be the *atmospheric pressure*, P_{atm} . So a special version of Dalton's law of partial pressures for use in fractional distillation will be

$$P_{\text{atm}} = P_A + P_B$$

Dalton and Raoult

If that's all there were to it, we'd be talking about Class 4: Steam Distillations and the like, where the components aren't soluble, and we could quit. Here, *the two are soluble in each other*. The individual vapor pressures of each component (P_A, P_B) depend not only on the temperature, but also on their **mole fraction**.

It makes sense, really. Molecules are the beasties escaping from solution during boiling, and, well, if the two liquids dissolve in each other perfectly, the more molecules (moles) of one component you have, the more the solution behaves like that one component, until it gets to be the same as a one-component liquid. This is Raoult's law

$$P_A = X_A P_A^\circ$$

where

P_A is the vapor pressure of A from the mixture

X_A is the mole fraction of liquid A

P_A° is the vapor pressure of the pure liquid A

If we change the As to Bs, can you still follow me? It's the same thing, only now with liquid B. If we combine the special case of Dalton's law with Raoult's law, we get

$$P_{\text{atm}} = X_A P_A^\circ + X_B P_B^\circ$$

Look at this. If there is NO B, then the fraction of A is 1, and the pure liquid A boils when its vapor pressure equals the atmospheric pressure. Didn't I say that? Similarly, for B without A, the mole fraction of B is 1, and it too boils when its vapor pressure equals the atmospheric pressure.

At this point, you're usually given the temperature versus mole fraction diagram for two miscible liquids (Fig. 175), and you're told it's a consequence of Raoult's law. Well, yes. But not directly. Raoult's law is a relationship of *pressure*, not temperature, versus mole fraction, and this law is pretty much straight line. You don't need all your orbitals filled to see that you've been presented with a *temperature versus mole fraction* diagram, there are *two lines* (not one), and neither of them is very straight.

A Little Algebra

I want to convert the combined laws of Dalton and Raoult so that I can show the variation in mole fraction explicitly. First, you'll agree that the mole fractions of A and B *must* add to 1 (or they wouldn't be fractions, eh?), so

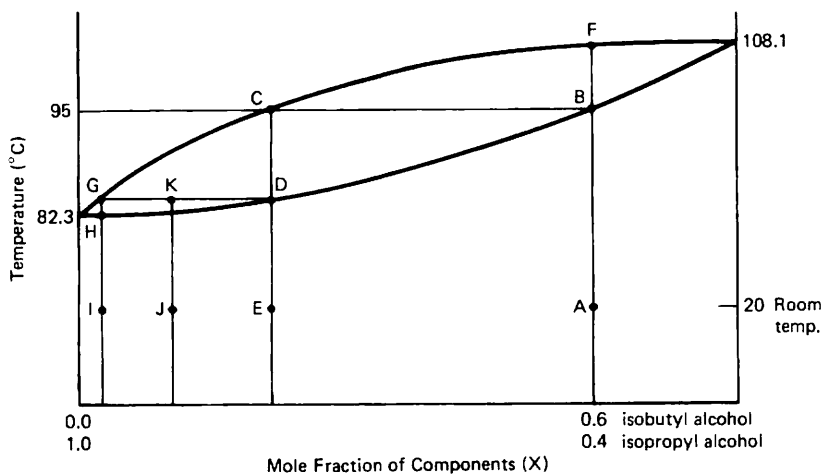


Fig. 175 Temperature-mole fraction diagram for the isobutyl-isopropyl alcohol systems.

$$X_A = X_B = 1$$

Now back with the Dalton and Raoult

$$P_{\text{atm}} = X_A P_A^\circ + X_B P_B^\circ$$

and seeing that $X_B = 1 - X_A$, I substitute to get

Expand this expression with a multiplication:

$$P_{\text{atm}} = X_A P_A^\circ + P_B^\circ - X_A P_B^\circ$$

Collect the terms with the mole fraction in them:

$$P_{\text{atm}} = X_A P_A^\circ - X_A P_B^\circ + P_B^\circ$$

And factor the mole fraction out to give:

$$P_{\text{atm}} = X_A (P_A^\circ - P_B^\circ) + P_B^\circ$$

To isolate the mole fraction X_A subtract P_B° from both sides:

$$P_{\text{atm}} - P_B^\circ = X_A (P_A^\circ - P_B^\circ)$$

and divide by $(P_A^\circ - P_B^\circ)$ to get

$$X_A = \frac{P_{\text{atm}} - P_B^\circ}{(P_A^\circ - P_B^\circ)}$$

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Clausius and Clapeyron Meet Dalton and Raoult

We still have a formula that relates mole fraction to pressure. Note, however, that with the exception of the atmospheric pressure (P_{atm}) *all* the other pressures are those of pure liquids (P_A° and P_B°). Now, how does the vapor pressure of a pure liquid vary with temperature? Smite your forehead and say that you could have had a V-8. The *Clausius–Clapeyron* equation:

$$p = p^\circ \exp \left\{ \frac{-\Delta H}{R} (1/T - 1/T^\circ) \right\}$$

The P° 's of Dalton–Raoult are vapor pressures taken at fixed temperatures. They are the p 's in the Clausius–Clapeyron equation found with a variation in temperature. You don't believe me? Pick a vapor pressure and temperature pair from Table 1 for either liquid, and let these be p° and T° (and don't forget to use K, not °C). Now what happens when the “unknown” temperature (T) is the same as T° ? The $(1/T - 1/T^\circ)$ becomes zero, the entire exponent becomes zero, p° is multiplied by 1 (anything to the power zero is 1, eh?), and so on $p = p^\circ$.

The next part is messy, but somebody's got to do it. I'm going to use the vapor pressure-temperature data for the normal boiling points of both liquids in the Clausius–Clapeyron equation. Why? They're convenient, *known* vapor pressure-temperature points. When I do this, however, I exercise my right to use different superscripts to *impress on you that these points are the normal boiling points*. So for liquid A, we have p_A° and T_A° ; if A is isobutyl alcohol, $p_A^\circ = 760$ torr and $T_A^\circ = 101.8^\circ\text{C}$. For liquid B, we have p_B° and T_B° ; if B is isopropyl alcohol, $p_B^\circ = 760$ torr and $T_B^\circ = 82.3^\circ\text{C}$.

Using the new letters on the previous page and substituting the Clausius–Clapeyron equation for every P° you get

$$\frac{P_{\text{atm}} - P_B^\circ \exp\left\{\frac{-\Delta H_B}{R}\left(1/T - 1/T_B^\circ\right)\right\}}{P_A^\circ \exp\left\{\frac{-\Delta H_A}{R}\left(1/T - 1/T_A^\circ\right)\right\} - P_B^\circ \exp\left\{\frac{-\Delta H_B}{R}\left(1/T - 1/T_B^\circ\right)\right\}}$$

Phew!

The only variables in this beast are the mole fraction (X) and the temperature (T). Every other symbol is a constant. We finally have the equation for the bottom line of the temperature-mole fraction diagram, something that has eluded us for years.

Dalton Again

What about the upper curve? Glad you asked (sigh). The composition in the vapor is also related to Dalton's law of partial pressures. For an ideal gas $PV = nRT$ (and you thought you'd never see that again!) and for the vapors above the liquid,

$$P_A = n_A \frac{RT}{V} \text{ and } P_B = n_B \frac{RT}{V}$$

Yet we know that the total pressure of Dalton's gang is the sum of their individual efforts:

$$P_{\text{Total}} = P_A + P_B$$

So,

$$P_{\text{Total}} = n_{\text{Total}} \left(\frac{RT}{V} \right)$$

Now watch, as I divide the pressure of A by the total pressure:

$$P_A / P_{\text{Total}} = n_A / n_{\text{Total}} \left(\frac{\frac{RT}{V}}{\frac{RT}{V}} \right)$$

Well, the RT/V s cancel giving

$$P_A / P_{\text{Total}} = n_A / n_{\text{Total}}$$

The ratio of the number of moles of A to the *total* number of moles is the **mole fraction of component A in the vapor**

$$X_A^{\text{Vapor}} = P_A / P_{\text{Total}}$$

P_{Total} for the ordinary distillation is the atmospheric pressure, 760 torr, (P_B 's, eh?). P_A is the vapor pressure of A, and again by Raoult's Law, $P_A = X_A P_A^\circ$. Putting the two together, we get

$$X_A^{\text{Vapor}} = X_A^{\text{Liquid}} P_A^\circ / 760$$

We can make the same kind of substitution of Clausius–Clapeyron here, and we get a similarly curved function for the upper line in the temperature-mole fraction diagram.

To show you that all this really does work, I've listed the experimental composition data for the isopropyl/isobutyl alcohol system from Landolt-Bornstein (Landolt-Bornstein is to physical chemistry what Beilstein is to organic. And wouldn't that make for a wild analogy question on the college board entrance exams?), along with my calculated data (Table 2). (That explains my choice of temperatures for Table 1.) I've also given the absolute and percent differences between the experimental data, and what I've calculated. These differences are on the order of 1% or less, a very good agreement indeed.

So now, for any two liquids, if you have their normal boiling points and vapor pressures at any other temperature, you can generate the temperature-mole fraction diagram.

Table 2 Experimental and Calculated Data.

Temperature vs. Mole Fraction Calculations		
Compound	Normal BP (C)	Vapor Pressure @ 100 (C)
2-Propanol	82.3	1440 torr
2-Methyl-1-propanol	108.2	570 torr
Data from Moore (3rd. ed.)		
Calculated ΔH (VAP)	2-Propanol	9515.73 cal/mol
	2-Methyl-1-propanol	10039.70 cal/mol

Comparison of Data from Moore and Calculated Data (T=100 (C))

		Moore	Calc.
Vapor pressures:	2-Propanol	1440	1440.05
(torr)	2-Methyl-1-propanol	570	570.02
Mole fraction:	2-Propanol	0.219	0.2184
(in liquid)	2-Methyl-2-propanol	0.781	0.7861
Mole fraction:	2-Propanol	0.415	0.4137
(in vapor)	2-Methyl-2-propanol	0.585	0.5863

Mole Fraction of 2-Propanol Liquid Data

#	T(C)	X Calc	X Lit.	Diff	% Diff
1	83.2	0.9458	0.9485	-.0027	-0.286
2	85.4	0.8213	0.8275	-.0062	-0.748
3	86.9	0.7425	0.7450	-.0025	-0.331
4	88.7	0.6540	0.6380	0.0160	2.505
5	90.9	0.5539	0.5455	0.0084	1.540
6	95.8	0.3591	0.3455	0.0136	3.949
7	99.9	0.2215	0.2185	0.0030	1.357
8	103.4	0.1191	0.1155	0.0036	3.096
9	106.2	0.0458	0.0465	-.0007	-1.507

Mole Fraction of 2-Propanol Vapor Data

#	T(C)	X Calc	X Lit.	Diff	% Diff
1	83.2	0.9785	0.9805	-.0020	-0.201
2	85.4	0.9228	0.9295	-.0067	-0.723
3	86.9	0.8820	0.8875	-.0055	-0.618
4	88.7	0.8300	0.8245	0.0055	0.663
5	90.9	0.7615	0.7580	0.0035	0.460
6	95.8	0.5880	0.5845	0.0035	0.600
7	99.9	0.4182	0.4270	-.0088	-2.063
8	103.4	0.2533	0.2510	0.0023	0.936
9	106.2	0.1070	0.1120	-.0050	-4.433

What Does It All Mean?

Getting back to the temperature-mole fraction diagram (Fig. 175), suppose you start with a mixture such that the mole fractions are as follows: isobutyl alcohol, 0.60, and isopropyl alcohol, 0.40. On the diagram, that composition is point A at a room temperature of 20°C. Now you heat the mixture, and you travel upward from point A to point B. The liquid has the same composition; it's just hotter.

At 95°C, point B, the mixture boils. Vapor, with the composition at point C, comes flying out of the liquid. (The horizontal line tying the composition of the vapor to the composition of the liquid is the **liquid-vapor tie-line**.), and this vapor condenses (point C to point D), say, part of the way up your distilling column.

Look at the composition of this *new liquid* (point E). It is *richer in the lower-boiling component*. The step cycle B-C-D represents one distillation.

If you heat this new liquid that's richer in isopropyl alcohol (point D), you get vapor (composition at point G along a horizontal tie-line) that condenses to liquid H. So step cycle D-G-H is another distillation. The two steps represent two distillations.

Much of this work was carried out using a special distilling column called a **bubble-plate column** (Fig. 176). Each *plate* really does act like a distilling flask with a very efficient column, and one distillation is really carried out on one physical plate. To calculate the number of plates (separation steps or distillations) for a bubble-plate column, you just count them!

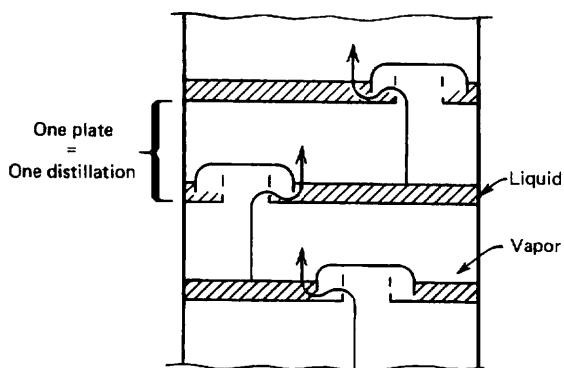


Fig. 176 A bubble-plate fractionating column.

Unfortunately, the fractionating column you usually get is not a bubble-plate type. You have an open tube that you fill with column packing (see “Class 3: Fractional Distillation” in Chapter 20) and *no plates*. The distillations up this type of column are not discrete, and the question of where one plate begins and another ends is meaningless. Yet, if you use this type of column, you do get a better separation than if you used no column at all. It’s as *if* you had a column with some bubble-plates. And if your distilling column separates a mixture as well as a bubble-plate column with two real plates, you must have a column with two **theoretical plates**.

You can calculate the number of theoretical plates in your column if you distill a two-component liquid mixture of known composition (isobutyl and isopropyl alcohol perhaps?) and collect a few drops of the liquid condensed from the vapor at the top of the column. You need to determine the composition of that condensed vapor usually from a calibration curve of known compositions versus their refractive indices [see Chapter 28, “Refractometry”], and you must have the temperature-mole fraction diagram (Fig. 171).

Suppose you fractionated that liquid of composition A, collected a few drops of the condensed vapor at the top of the column, analyzed it by taking its refractive index, and found that this liquid had a composition corresponding to point J on our diagram. You would follow the same path as before (B-C-D, one distillation; D-G-H, another distillation) and find that composition falls a bit short of the full cycle for distillation #2.

Well, all you can do is estimate that it falls at, say, a little more than halfway along this second tie-line, eh (point K)? OK then. This column has been officially declared to have 1.6 theoretical plates. Can you have tenths of plates? Not with a bubble-plate column, but certainly with any column that does not have discrete separation stages.

Now you have a column with one-point-six theoretical plates. “Is that good?” you ask. “Relative to what,” I say. If that column is 6 feet high, that’s terrible. The Height Equivalent to a Theoretical Plate (HETP) is 3.7 feet/plate. Suppose another column also had 1.6 theoretical plates, but was only 6 inches (0.5 feet) high. The HETP for this column is 3.7 inches/plate, and *if it were 6 feet high*, it would have 19 plates. The *smaller* the HETP, the more efficient the column is. There are more plates for the same length.

One last thing. On the temperature-mole fraction diagram, there’s a point F that I haven’t bothered about. F is the grade you’ll get when you extend the A-B line up to cut into the upper curve and you then try to do anything with this point. I’ve found an amazing tendency for some people

to extend that line to point F. Why? Up the temperature from A to B, and the sample boils. *When the sample boils, the temperature stops going up.* Heat going into the distillation is being used to vaporize the liquid (heat of vaporization, eh?) and all you get is a vapor, enriched in the lower-boiling component, with the composition found at the end of a *horizontal* tie-line.

Reality Intrudes I: Changing Composition

To get the number of theoretical plates, we fractionally distilled a known mixture and took off a small amount for analysis, so as not to disturb things very much. You, however, have to fractionally distill a mixture and hand in a good amount of product, and do it within the time limits of the laboratory.

So when you fractionally distill a liquid, you *continuously* remove the lower-boiling fraction from the *top* of the column. And where did that liquid come from? The boiling fluid at the *bottom* of the column. Now if the distillate is richer in the lower-boiling component, what happened to the composition of the boiling liquid? I'd better hear you say that the boiling liquid gets richer in the *higher-boiling* component (Fig. 177).

So as you fractionally distill, not only does your boiling liquid get richer in the higher component, but so also does your distillate, your condensed vapor. Don't worry too much about this effect. It happens as long as you have to collect a product of revaluation. Let your thermometer be your guide, and keep the temperature spread less than 2°C.

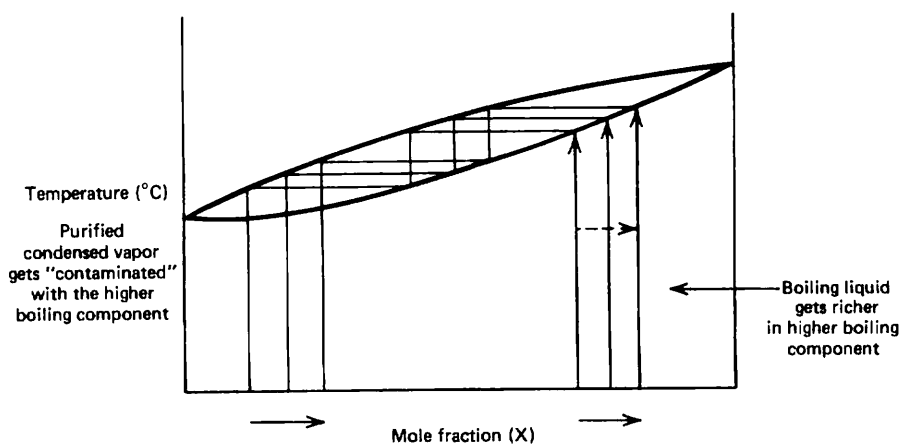


Fig. 177 Changing composition as the distillation goes on.

Reality Intrudes II: Nonequilibrium Conditions

Not only were we forced to remove a small amount of liquid to accurately determine the efficiency of our column, but also we had to do it *very slowly*. This allowed the distillation to remain *at equilibrium*. The **throughput**, the rate at which we took material out of the column, was *very low*. Of all the molecules of vapor that condensed at the top of the column, *most fell back down the column; few were removed*. A very high **reflux ratio**. With an infinite reflux ratio (no throughput), the condensed vapor at the top of the column is as rich in the lower-boiling component as it's ever likely to get in your setup. As you remove this condensed vapor, the equilibrium is upset, as more molecules rush in to take the place of the missing. The faster you distill, the less time there is for equilibrium to be reestablished and the less time there is for the more volatile components to sort themselves out and move to the top of the column. So you begin to remove higher-boiling fractions as well, and you cannot get as clean a separation. In the limit, you could remove vapor so quickly that you shouldn't have even bothered using a column.

Reality Intrudes III: Azeotropes

Occasionally, you'll run across liquid mixtures that cannot be separated by fractional distillation. That's because the composition of the vapor coming off the liquid is the *same* as that of the liquid itself. You have an **azeotrope**, a liquid mixture with a constant boiling point.

Go back to the temperature-mole fraction diagram for the isopropyl alcohol-isobutyl alcohol system (Fig. 175). The composition of the vapor is *always different from* that of the liquid, and we can separate the two compounds. If the composition of the vapor is the same as that of the liquid, that separation is hopeless. Since we've used the notions of an ideal gas in deriving our equations for the liquid and vapor compositions (Clausius–Clapeyron, Dalton, and Raoult), this azeotropic behavior is said to result from *deviation from ideality*, specifically *deviations from Raoult's law*. Although you might invoke certain interactive forces in explaining nonideal behavior, you cannot predict azeotrope formation *a priori*. Very similar materials form azeotropes (ethanol–water). Very different materials form azeotropes (toluene–water). And they can be either **minimum-boiling azeotropes** or **maximum-boiling azeotropes**.

Minimum-Boiling Azeotropes

The ethanol-water azeotrope (95% ethanol–5% water) is an example of a minimum-boiling azeotrope. Its boiling point is lower than that of the components (Fig. 178). If you've ever fermented anything and distilled the results in the hopes of obtaining 200 proof (100%) white lightning, you'd have to content yourself with getting the azeotropic 190 proof mixture instead. Fermentation usually stops when the yeast die in their own 15% ethanol solution. At room temperature, this is point A on our phase diagram. When you heat the solution, you move from point A to point B and, urges to go to point F notwithstanding, you cycle through distillation cycles B–C–D and D–E–G. And, well, guess what comes off the liquid? Yep, the azeotrope. As the azeotrope comes over, the composition of the boiling liquid moves to the right (it get richer in water), and finally there isn't enough ethanol to support the azeotropic composition. At that point, you're just distilling water. The process is mirrored if you start with a liquid that is >95% ethanol and water. The azeotrope comes off first.

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Maximum-Boiling Azeotropes

The chloroform-acetone azeotrope (52% chloroform–48% acetone) is an example of the much rarer maximum-boiling azeotrope. Its boiling point is higher than that of the components (Fig. 179). At compositions off the

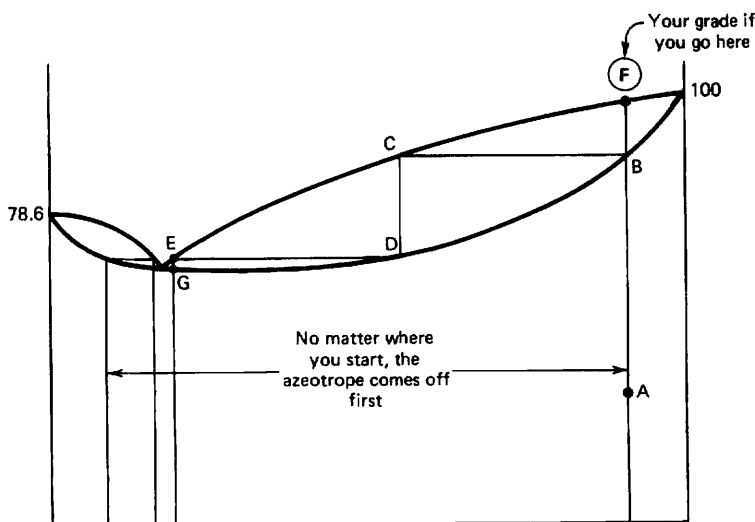


Fig. 178 Minimum-boiling ethanol–water azeotrope.

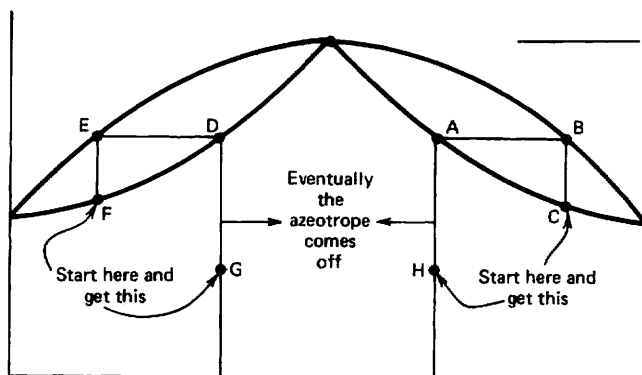


Fig. 179 Maximum-boiling chloroform-acetone azeotrope.

azeotrope, you do distillations A-B-C or D-E-F (and so on) until the boiling liquid composition reaches the azeotropic composition. Then that's all that comes over. So, initially, one of the components comes off first.

Azeotropes on Purpose

You might think the formation of azeotropes is an unalloyed nuisance, but they can be useful. Toluene and water form a minimum-boiling azeotrope (20.2% water; 85°C). If for some reason, you need *very dry* toluene, all you have to do is distill some of it. The water-toluene azeotrope comes off first, and, well, there goes all the water. It gets removed by **azeotropic distillation**. The technique can also be used in certain reactions, including the preparation of amides from very high-boiling acids and amines. (They can even be solids.) You dissolve the reagents in toluene, set up a reflux condenser fitted with a **Dean-Stark trap** (Fig. 180), and let the mixture reflux. As the amide forms, water is released and the water is constantly removed by azeotropic distillation with the toluene. The azeotrope cools, condenses, and collects in the Dean-Stark trap. At room temperature, the azeotrope is said to "break," and the water forms a layer at the bottom of the trap. Measure the amount of water, and you have an idea of the extent of the reaction.

Absolute (100%) ethanol is often made by adding benzene to the ethanol-water **binary azeotrope** (two components) to make a **ternary azeotrope** (three components). This ternary alcohol-water-benzene (18.5:7.4:74.1) azeotrope comes over until all the water is gone, followed by a benzene-ethanol mixture. Finally, absolute ethanol gets its chance to appear, marred only slightly by traces of benzene.

Other Deviations

The furfural-cyclohexane phase diagram (Fig. 181) shows that you can have mixtures that exhibit nonideal behavior without having to form an azeotrope. In sum, without the phase diagram in front of you, you shouldn't take the distillation behavior of any liquid mixture for granted.

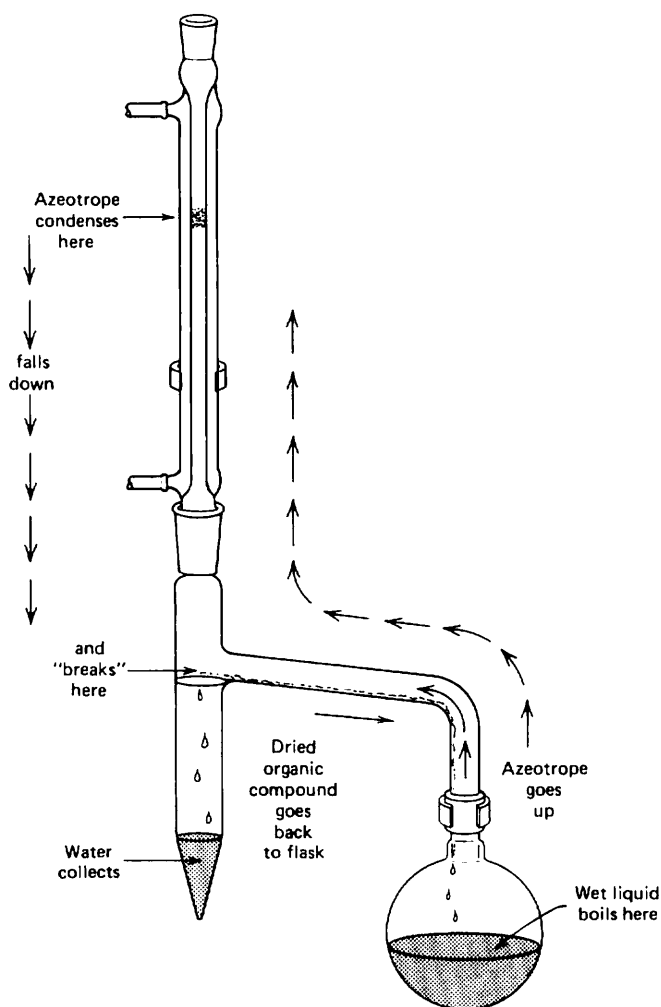


Fig. 180 Removing water by azeotropic distillation.

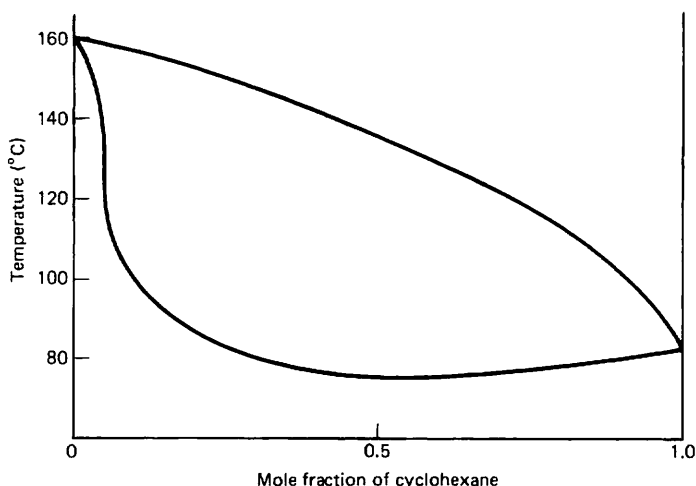


Fig. 181 Other deviant behavior (but no azeotropes) in the furfural–cyclohexane system.

CLASS 4: STEAM DISTILLATION

Steam distillation is for the separation of mixtures of tars and oils, and they must not dissolve much in water. If you think about it a bit, this could be considered a fractional distillation of a binary mixture with an *extreme* deviation from Raoult's law. The water and the organic oils want nothing to do with each other. So much so, that you can consider them unmixed, in separate compartments of the distilling flask. As such, they act completely independently of each other. The mole fraction of each component in its own compartments is 1. So Raoult's Law becomes

$$P_{\text{Total}} = P_A + P_B$$

This is just Dalton's Law of partial pressures. P_{Total} is P_{atm} for a steam distillation. So the vapor pressure of the organic oil is now less than that of the atmosphere and the water, and codistills at a much lower temperature.

As an example, suppose you were to try to directly distill quinoline. Quinoline has a boiling point of 237°C at 1 atm. Heating organic molecules to these temperatures may often be a way to decompose them. Fortunately, quinoline is insoluble in water, and it does have some vapor pressure at about the boiling point of water (10 torr at 99.6°C). If it had a *much lower*

vapor pressure at the boiling point of water (say, 0.1 torr), there couldn't be enough of it vaporizing to make even steam distillation worthwhile.

Well, at 99.6°C, quinoline contributes 10 torr to the total vapor pressure, and water must make up the difference (750 torr) in order to satisfy Dalton's Law of partial pressures to make P_{Total} 760 torr at boiling. Using the relationships for the composition of the vapor *over a liquid*, we can calculate the quinoline/water ratio coming over.

If we consider each to be an ideal gas, then

$$PV = nRT \text{ (yes, again)}$$

The number of moles (n) of anything is just the weight in grams (g) divided by the *molecular weight* of that substance (MW), and so

$$PV = (g / \text{MW})(RT)$$

Multiplication by MW gives

$$(\text{MW})PV = g(RT)$$

and isolating the mass of the material by dividing by RT gives

$$(\text{MW})PV / RT = g$$

Now for *two* vapors, A and B, I'll construct a ratio where

$$\frac{(\text{MW})_A P_A V / RT = g_A}{(\text{MW})_B P_B V / RT = g_B}$$

With A and B in the same flask, R, T, and V must be the same for each, and we can cancel these terms giving

$$\frac{(\text{MW})_A P_A = g_A}{(\text{MW})_B P_B = g_B}$$

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If we plug in values for the molecular weights and vapor pressures of quinoline and water, we get

$$\frac{(129)(10)}{(18)(750)} = \frac{0.0956}{1}$$

So, as an approximation, for every 10 *g* of distillate we collect, 1 *g* will be our steam-distilled quinoline.